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(12) **Patent:**(11) **CA 901727**(54) **PROCESS FOR CONTINUOUS POLYMERIZATION**

(54)

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(72) **Inventors (Country):** **HERBERT AMANN** (Not Available)  
**WOLFGANG SIBENHORN** (Not Available)  
**ERICH BADER** (Not Available)

(73) **Owners (Country):** **DEUTSCHE GOLD- UND SILBER-  
SCHEIDEANSTALT VORMALS ROESSLER**

(71) **Applicants (Country):**

(74) **Agent:**

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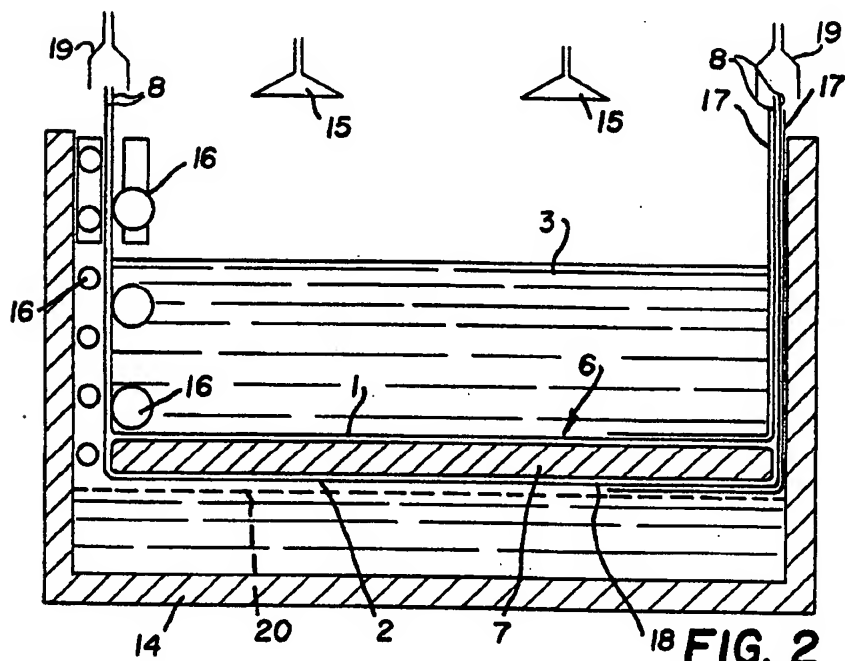
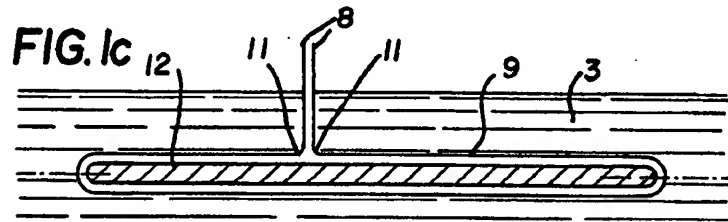
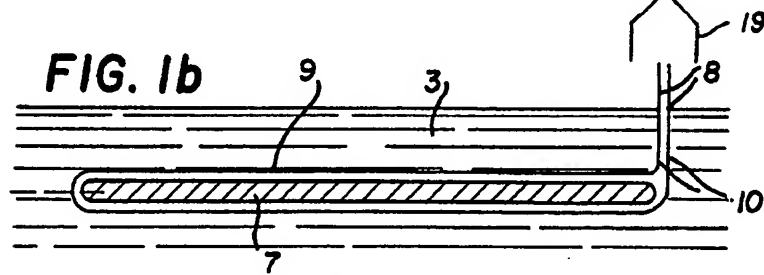
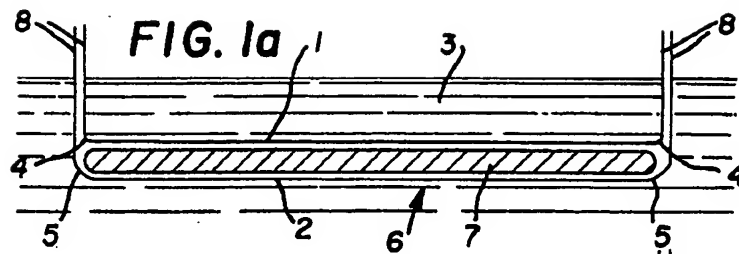
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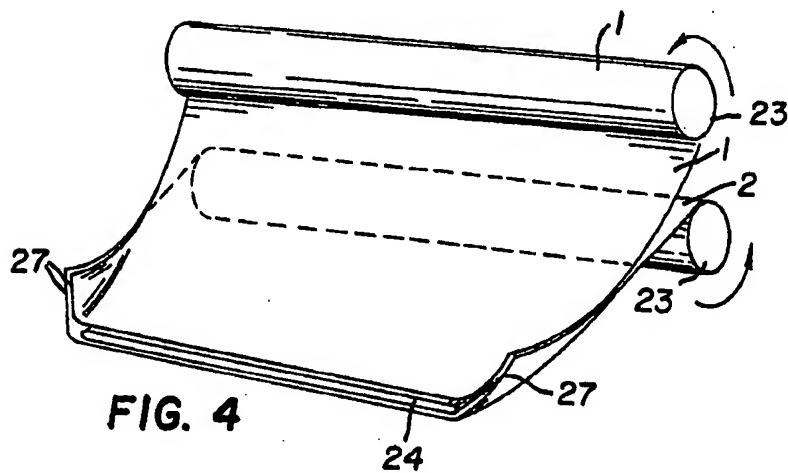
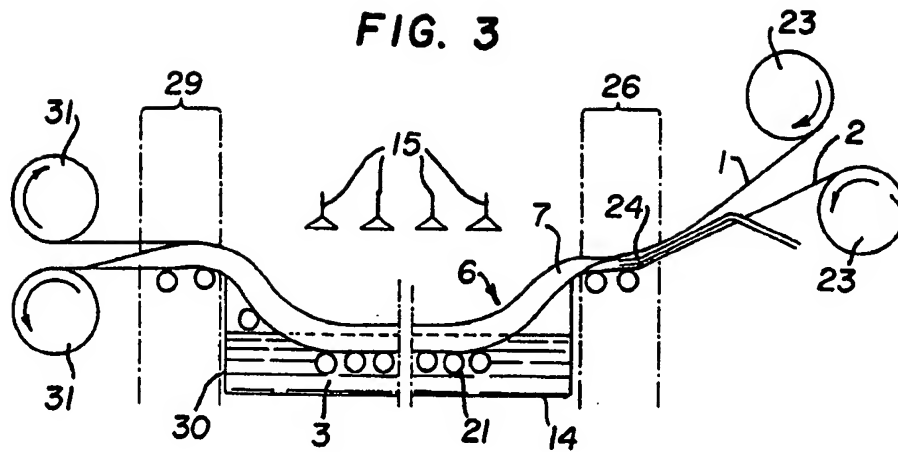
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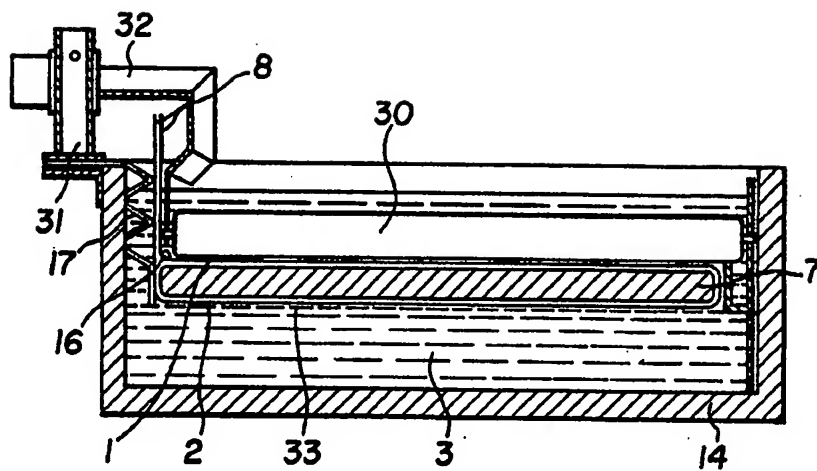
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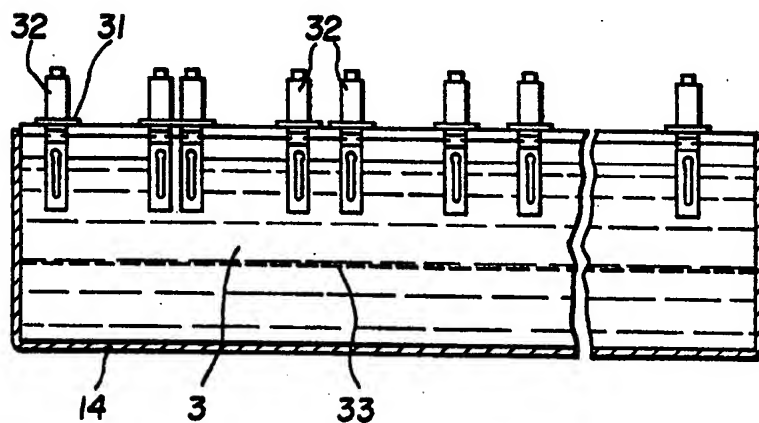


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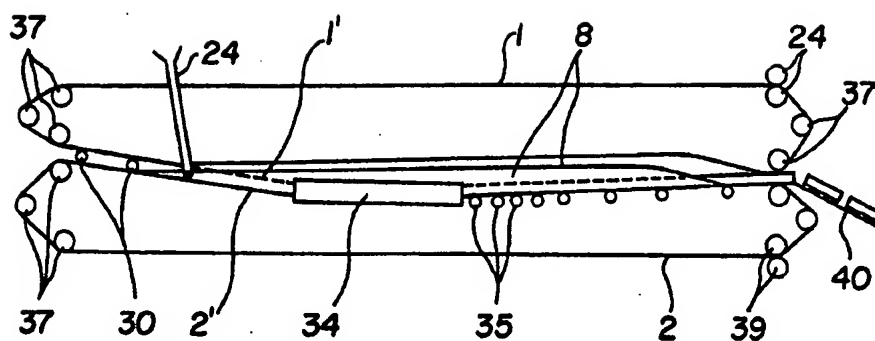


**FIG. 5**

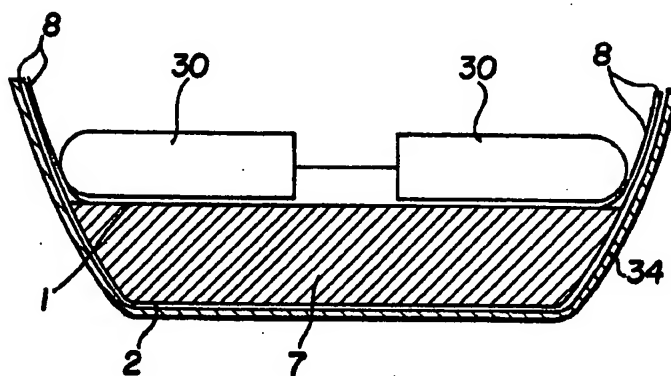


**FIG. 6**

*H. Amann  
E. Baden  
W. Lienhard  
Marks & Clerk*



**FIG. 7**



**FIG. 8**

*H. Amann  
E. Bader  
W. Libenhorn*

*Marks & Clerk*

The invention relates to a process for continuously carrying out polymerizations.

It is known to carry out continuous polymerization of trioxane, if required, in the presence of known comonomers, by polymerizing the trioxane with cationic catalysts, with the exclusion of air or oxygen, in plastic tubing, by pouring the polymerization mixture into a plastic tube, continuously passing the filled tube through a liquid bath having the polymerization temperature or through a heating channel and, if required, subsequently passing the tube through a cooling bath.

The above process may be carried out in such a manner that, for example, a plastic tube is produced by joining and welding together one or two preformed plastics sheets, the welding being performed shortly after passing a feed hopper for the polymerization mixture. However, a finished tube may also be used, and is slit shortly after passing the point of feeding, whereupon it is welded together again. In any event, the tube is again cut open after complete polymerization, and the polymer is removed. After further extrusion, the plastic tube may be used again, but this means an additional operation. However, in the process it is also possible to cut the tube open in such a manner that it can be immediately used again, but in such cases it is frequently required to prepare the marginal zones for further welding. If the tube is to be closed by welding, then only weldable materials can be used, but their resistance to high temperature is of course limited (see German Patent No. 1,244,408).

It is the object of the present invention to provide other means for the polymerization. In addition, the present invention provides the possibility of enlarging the choice of tube materials to be used for carrying out the known process and



of improving their reusability.

Accordingly, the present invention provides a process for producing homopolymers or copolymers by continuous polymerization using polymerization initiators by continuously pouring a polymerization mixture into a continuously moving jacket of a flexible material with substantially complete displacement of air. The jacket is flat in the region of the feed point. The jacket is then passed through a zone having the polymerization temperature and, if required, subsequently through a cooling bath, the forming of the flexible material into a jacket being continuous. The process is characterized by the joining of two separate sheets of a flexible material in the region of the feed device, so that they are stacked flat and enclose the feed device between them, or only one sheet of such material is folded in the region of the feed device along one line or along two lines in such a manner that a flat double sheet is formed, which encloses the feed device and, upon passing the feed device, the open stacked and longitudinally extending marginal zones of the upper and lower sheets or of the folded sheet are joined together and bent upwardly with the aid of a guide device to form a jacket which serves as a liquid-tight tube or jacket during polymerization. The jacket can form two troughs fitted into one another, the mixture to be polymerized filling the bottom of the lower trough and the side walls of the two troughs converging or being pulled up above the polymerizable mixture, or the jacket can form a slit tubular structure having converging edges, the tube edges extending beyond the polymerizable mixture and being pulled up as well.

Thus, according to the process of the present invention the jacket serving as the liquid-tight tube is formed by simple molding of the flexible material at its marginal zones



without permanent sealing by welding, sewing, bonding or clamping. The usual expenditure for apparatus is reduced and the choice of usable flexible materials is substantially greater, since it is no longer necessary to take into account the properties required for carrying out the conventional sealing methods. This is of special advantage because of the greater possibilities for variation in the selection of the of the temperatures for polymerization and possibly for further heating or cooling stages. Moreover, since the sheet or sheets  
10 are not permanently sealed, re-use of the tube material is facilitated. For example, the material can be unrolled from a roll on one side of the polymerization device, joined to form a jacket and, upon leaving the polymerization device, the material can again be rolled onto a roll in a simple manner. The rolling device simultaneously passes the jacket through the polymerization zone and, if required, through further tempering zones. The material is then immediately available for re-use. It is also possible to convey the sheet as an endless strip instead of repeatedly unrolling and rolling the sheet. It has  
20 been found to be especially favourable that no special extractors are required for opening the jacket and separating it from the polymerized material. Of course, the removal of the jacket may also be dispensed with and the jacket may be used as packaging material.

In this process, it is surprising and unexpected that, even with continuous movement, a liquid-tight structure forms simply by bending the marginal zones of the sheets upwardly, i.e., without attaching a permanent seal. One would have expected that leaks would have formed due both to the variable  
30 stretching strain of the various sheet sections over the relatively greater linear extension of the polymerization zone and to the transition of the jacket content from the liquid state to the

solid, and that cracks would form in the thin jacket materials.

The invention will now be described in greater detail with reference to the accompanying drawings, wherein;

Figure 1a is schematic cross sectional view of a polymerization jacket or tube formed by two sheets of flexible material;

Figures 1b and 1c are schematic cross sectional views of polymerization jackets formed by one sheet of flexible material;

10        Figure 2 is a schematic cross sectional view of an apparatus for polymerizing using the jacket of Fig. 1a;

Figure 3 is a schematic cross sectional view similar to Fig. 2, showing an apparatus for feeding sheets for forming a jacket;

Figure 4 is a perspective view of a portion of the apparatus of Figure 3;

Figure 5 ~~cross~~ sectional view of a cooling bath with a guide device for use in the apparatus of the present invention;

20        Figure 6 is a longitudinal sectional view of the cooling bath of Figure 5;

Figure 7 is a schematic side view of a complete polymerization apparatus in accordance with the present invention; and

Figure 8 is a schematic cross sectional view of a trough portion of the apparatus of Figure 7;

30        With reference to the drawings, and in particular to Fig. 1a, two sheets of material 1 and 2 are placed in a polymerization bath 3, and the sheets 1 and 2 are bent upwardly at 4 and 5, respectively, to form a generally U-shaped jacket 6 for a polymerizable mixture 7, portions 8 of the sheets 1 and 2 extending upwardly in parallel relationship to each other out

of the bath 3. A pair of alternative arrangements are shown in Figs. 1b and 1c in which a single sheet 9 is folded around the polymerizable mixture 7 in the bath 3 and bent upwardly either at one side 10 to form a generally L-shaped jacket of the mixture 7 or at a location 11 along the top surface 12 of the mixture 7 to form a generally inverted T-shaped jacket for the mixture 7. The portions 8, of the sheet(s) extending upwardly out of the bath are parallel and, when folded, at their side edges, form a liquid-tight seal. The portions 8 form air  
 10 intake channels.

While the folds at 4, 5 and 11 are shown as right angles, such folds may form an acute or obtuse angle with a horizontal plane through the polymerizable mixture 7. Since the side portions 8 of the jacket slope downwardly and the polymerization zone extends horizontally in the bath 3, laws concerning communicating tubes must be observed when deciding the dimensions of the channels formed by the side portions 8.

With reference to Fig. 2, the portions 8 of the sheet(s) are bent upwardly by means of guides or forming devices, for example, forming jigs, rods or rollers. As shown in Fig. 2  
 20 the sheets 1 and 2 forming the jacket are passed through a long trough 14 containing the liquid bath 3. The jacket 6 may be passed through an air bath. The temperature in bath 3 is adjusted by spraying a liquid into the bath from nozzles 15 located above the bath.

Shaping of the sheets 1 and 2 into a jacket 6 is performed by guide rods 16, which may be rolls or rollers, and/or by forming jugs 17. Various combinations of shaping devices are possible. The bottom surface 18 of the jacket 6  
 30 is supported by a perforated plate 20, which may be placed with spaced rolls 21 (see Fig. 3). A similar plate or rolls may be provided above the jacket 6 in the bath 3. When using only

one sheet 9 to form the jacket, the guide devices 16 and/or 17 may be replaced by a single guide at the location of the fold. Since the sheets are formed of quite flexible material, the guiding or forming devices can be correspondingly lightweight. When using a liquid bath, the forming devices can, in many cases, be installed at only a few points in the bath.

The apparatus shown in Fig. 3 is similar to that of Fig. 2 with rolls 21 supporting the bottom surface 18 of the jacket 6. The sheets 1 and 2 used for forming the jacket 6 are dispensed from rolls 23, and come closest together downstream of a nozzle 24 for feeding polymerizable material 7 into the jacket 6. In a region 26, containing the nozzle 24, the side edges 27 of the sheets 1 and 2 are bent upwardly by guide devices (not shown), and a liquid tight jacket 6 is formed. The folding of the sides 27 of the sheets 1 and 2 is clearly shown in Fig. 4. In the region 26, the jacket 6 slopes downwardly into the bath 3, and thus filling with a liquid polymerization mixture 7 is possible, with virtually complete displacement of air.

When using a liquid bath, the upturned edges 27 of the sheets 1 and 2 project upwardly beyond the surface of the bath 3. The guide devices (not shown), which may be provided above the entire length of the trough 14, extend to a region 29, which follow the trailing end 30 of the trough 14. Upon leaving the trough 14, the sheets 1 and 2 are flattened, and rolled onto rolls 31. When using endless sheets, the sheets 1 and 2 pass around the rolls 31 and are returned to the rolls 23 for re-use. Before entering the region 29, the jacket 6 may pass through a tempering zone (not shown). When using only one sheet of flexible material the pairs of rolls 23 and 31 are replaced by single rolls. Before entering the region 29, the sheet is folded along its centre line or along a line

parallel thereto using conventional devices.

The jacket 6 is filled with the polymerization mixture a feed device (s), for example, a tube (s), a hose (s), or a trough(s), which is inserted between the sheets prior to joining. Such devices extend to the region of the jointly upturned marginal side edges.

If the jacket 6 slopes downwardly, the polymerization mixture flows into the jacket 6 to fill it. Since the jacket 6 consists of flexible material, it may assume virtually any cross sectional configuration, or it may be given any cross, sectional configuration using guides or forming devices. When using a liquid bath, there may be some buoyancy, especially prior to the polymerization. This is due to differences in density of the liquid bath and that of the filled jacket. In such case, the submersion of the jacket 6 must be brought using devices, for example baffles. Such devices may simultaneously serve for shaping the polymer to be produced. The emission of the polymerization heat is promoted if the filled jacket 6 assumes a flat, virtually rectantular cross section, i.e., if the ratio of the thickness to width is at least 1:3. For example, at a width of the jacket 6 of approximately 10 to 15 cm, such ratio may be 1:10 and at a width of approximately 150 cm it may be 1:100.

The joining of the sheets to form a jacket may be further facilitated by the concomitant use of an agent which increases the adhesion of the side edges, for example, the marginal edges may be entirely or partially provided with a soft adhesive. The polymerization mixture itself may act as a soft adhesive, as is frequently the case in solutions of polymers, for example, in monomers. Especially when using an air bath, electrostatic charging may be utilized for the same purpose.

Flexible non-metallic materials which have no dimensional stability, i.e., those which cannot keep a specific permanent shape without additional auxiliary agents are used as flexible materials for the sheets. For example, if the sheets are made tub-shaped with a circular cross section using auxiliary agents, they collapse upon removal of the auxiliary agents and form a flat tube. Of course, under the conditions of the process the flexible materials must be durable and inert. For example, any sheet in the unstretched or stretched state, which is inert under polymerization conditions and does not adhere to the polymer, may be used. Typical examples are polyalkylenes such as polyethylene, polypropylene, polyterephthalate, cellulose ester and cellulose ether, polyamide, polyurethanes, silicones, fluorine-containing plastics, reinforced sheets, for example, those of polytetrafluoroethylene reinforced with glass fibres, and composite sheets or varnished sheets, non-weldable sheets, for example, cellulose hydrate-polyethylene composite sheets, cellulose hydrate sheets with a varnish layer, plastics-coated or impregnated paper, varnished paper, etc. Because of their high tensile strength, coated fabrics or fleeces, for example, cotton fabrics with silicone coating, polyester fabrics with polyurethane coating, metal-coated fabrics, etc., are well suited for use in the present invention. The wall thickness of the flexible material usually is between approximately 0.03 and approximately 2.0 mm. However, wall thicknesses beyond this range are also suitable.

If the polymer adheres to the jacket as it sometimes happens with the jacket material, this may be avoided by providing the jacket with a known mold release agent (for example, silicone oil). This may be done, for example, by spraying.

Because of the longer service life and the lower wear, thicker and qualitatively more valuable material can be used for the jacket since such a material can usually be more intensely stressed mechanically and can be taken off faster.

When using two sheets (for example, according to Figure 1a) it is, of course, possible that the two sheets have different thicknesses; they may also be of different materials.

Likewise, it is also possible in the various embodiments to use a double sheet instead of one sheet, i.e.,  
 10 two superjacent sheets (according to Figure 1a there would then be a total of four sheets and according to Figure 1b two sheets) which may have in turn different thicknesses and consist of different materials. For example, a thinner and non-adhesive sheet may be chosen as the inner sheet in contact with the polymer and a thicker sheet is chosen as the outer sheet, which is more intensely stressed mechanically, irrespective of possible adhesion to the polymer. These possibilities are also important if the sheet is to be used for packaging.

When using a double sheet the inner sheet may  
 20 consist of a metallic material, for example, in the form of a metal mesh, whereby an improved heat conduction is obtained under certain conditions.

The process according to the invention is quite generally suitable for the continuous polymerization of fluid materials, irrespective of their nature. The process is especially suitable when solid polymers form. However, it is most suitable for the homopolymerization and copolymerization  
 A of compounds with polymerizable <sup>oxygen</sup> ~~oxygen~~ functions such as, for example, ethers, acetals, ketals, esters, etc. This includes  
 30 primarily compounds which contain at least one C-O-C bond in cyclic or linear arrangement such as, for example, cyclic aliphatic or cyclic araliphatic acetals, especially formals or ketals, more specifically those of aliphatic diols and

oxadiols such as 1,3-dioxolane, 1,3-dioxo-cycloheptane, 1,3,6-trioxa-ctane, trioxane, tetroxane, trioxepane; cyclic aliphatic or cyclic araliphatic esters, for example, lactones; cyclic aliphatic or cyclic araliphatic ethers, such as ethylene oxide, epichlorohydrin, other olefin oxides, tetrahydrofuran, styrene oxide or other polymeric esters, acetals and ethers such as polydioxolane, polyepoxides, copolymers of trioxane and ethylene oxide, etc. As the last examples show, the compounds to be polymerized may already be

10 in the form of polymers (prepolymers).

The most important use lies in the polymerization of trioxane or tetroxane either by a homopolymerization or copolymerization. For the copolymerization of trioxane and tetroxane especially comonomers or even polymeric compounds may be used which result in poly-oxymethylenes with interspersed oxyalkylene units (alkylene: at least 2 carbon atoms, preferably 2 to 5 carbon atoms) such as, for example, the above-mentioned cyclic acetals, ethers or polymeric acetals and ethers. The mixing proportion of the starting components is

20 arbitrary.

However, comonomers and compounds which are known for the copolymerization of trioxane may be used, for example, substances having a carbon to carbon double or triple bond such as styrene, acrylonitrile, copolymers of methyl methacrylate and styrene, etc. Moreover, the addition of chain-transfer agents by means of which stable terminal groups are incorporated is possible. For example, aliphatic or araliphatic or aromatic linear ethers (e.g. dibenzyl ether, diisopropyl ether), acetals, ketals, esters or anhydrides are

30 chain-transfer agents of this kind.

Apart from the addition of substances which participate in the polymerization it is of course possible



to add plasticizers, a variety of stabilizers, dyes, pigments, fillers, expanding agents, regulators, etc.

According to the process of the present invention, substances which constitute polymers (for example, prepolymers of trioxepane) can be further polymerized to higher molecular weights. However, this would require that the prepolymer is fluid or liquid or will be fluid at moderate temperatures or that it is soluble in a second fluid or liquid substance (usually a monomer). It is also possible to use substances  
10 containing more than one polymerizable group as comonomers or prepolymers and to obtain cross-linking products in this manner.

The process according to the invention is especially suitable for polymerizations which are sensitive to atmospheric influences (humidity of the air, CO<sub>2</sub>, oxygen) such as, for example, cationic polymerizations, especially those of trioxane and tetroxane.

The polymerization is initiated by means of known initiators: cationic, anionic or radical initiators or energy-bearing radiation. For the polymerization of oxacyclic  
20 compounds or polymeric compounds with C-O-C bonds especially ionic (cationic or anionic) catalysts are used. In the case of cyclic ketals and acetals, especially cationic initiators such as, for example, protone acids, Lewis acids; H-acidic acids with complex anion such as, for example, perchloric acid, HBF<sub>4</sub>; oxonium salts; perchloric esters; perchloric anhydrides, etc., are used. The process is also very suitable when using very active initiators, such as perchloric acid or perchloric acid derivatives, as well as fluorine-containing catalysts, for example, antimony pentafluoride and its complexes.

30 A homogeneous liquid mixture of the reactants, which is produced only shortly before it is charged into the jacket, is suitably used as the starting mixture. The

retention time of the ready mixture in the mixer must then be so adjusted, by controlling the feed of the individual components and the discharge of the ready homogeneous mixture, that the mixture is still fluid or thinly liquid when charging the jacket.

10 A modification of the process according to the invention lies in that instead of first mixing a solution of the catalyst with the mixture to be polymerized this solution is sprayed onto the inside of the jacket prior to adding the mixture to be polymerized, so that the inner wall of the jacket is to some extent impregnated with the finely divided catalyst. Moreover, the catalyst may also be spread on the inside of the jacket in the form of a solution or paste. In order to achieve a uniform distribution of the catalysts in the mixture to be polymerized, the jacket may be passed through several tandem-joined double rolls and may thus be intensely kneaded, for example, prior to feeding the mixture to be polymerized.

20 When using less active initiators, for example, boron trifluoride or derivatives thereof, it is possible, in many cases, to achieve an increase in the reaction rate by subsequent tempering in the tube, for example, at temperatures between 70 and 80°C.

For the production of foamable polymers, known expanding agents are added to the starting mixture.

The process of the present invention also admits subsequent additions and subsequent dosing (for example, initiator, expanding agents, coloring agents, injection of gases, etc.) as long as the content of the jacket is in a state  
30 which permits homogeneous mixing.

Moreover, it is possible to extract residual monomers and, for example, even formaldehyde, over the ends

of the marginal zones (for example, over the points 8 of Figures 1a to 1c or of Figure 2) by means of suction devices 19 (see Figs. 1b and 2), and, if required, to return these substances by recycling them to the starting mixture.

Thus, for example, in polymerizations in which one or several of the starting materials escape to some extent during polymerization, it is possible to use an excess of these components from the outset, so that in the final effect the proportion of the components is always as desired due to the continuous process.

Upon carrying out the process of the present invention, the procedure may be such that the initiator is added to the substance to be polymerized either immediately prior to the polymerization or continuously, for example, by injecting with a pump or by way of a mixer, for example, a colloid mill. When using prepolymers the initiator still present from their production and possibly also regulators may be used or replenished. If fast-acting initiators are used, then the procedure may be such that, for example, the substance to be polymerized is divided into two portions and that only the components of the initiator system which produce mixtures having a sufficiently long storage life are added to each of these portions. The two portions are then combined, this may be done by joining two feed pipes. The material is continuously placed in the jacket in this state and in such amounts that air is virtually completely displaced therefrom. This can also be done with the concomitant use of a protective gas. The rate of dosing the liquid or fluid mixture to be polymerized is suitably adapted to the layer thickness in such a way that as much mixture is added as solid polymer is removed. The filled tube is then passed through an air bath or preferably through a liquid bath, which has the

required polymerization temperature. The polymerization is completed while the jacket passes through the bath. The rate of passage, as a function of the polymerization heat set free, is suitably adjusted to the length of the tempering bath or cooling bath; with given length of the tempering bath and with intense reaction heat or long-lasting reaction heat, e.g., the rate of passage will be slowed down and vice versa the tempering bath may of course be correspondingly extended. Upon leaving the tempering bath, the tube may also be passed  
 10 through a tempering zone, whereupon the polymer can be removed from the sheets, which have been unfolded, and the polymer may be crushed. However, it is also possible to so guide the filled jacket in the bath and to so shape it that molded pieces, for example, plates or sections, are obtained immediately as a final product. Shaping suitably takes place only shortly before solidification of the polymerization mixture.

The perchlorate initiators for the use of which (apart from other initiators) the process according to the  
 20 invention is especially suitable are described in more detail below.

This relates primarily to perchloric esters, chiefly with aliphatic alcohols such as, for example, tertiary butyl perchlorate, methoxy-methyl perchlorate, or with aromatic or araliphatic alcohols, such as triphenyl-methyl perchlorate, methyl-diphenyl-methyl perchlorate, dimethyl-phenyl-methyl perchlorate; to perchloric anhydrides, chiefly to anhydride of perchloric acid and to carboxylic acids such as acetyl perchlorate, benzoyl perchlorate, to ether or ketone perchlorates as well as to inorganic perchloric acid derivatives such  
 30 as those mentioned, for example, in Gmelins Handbuch der Organischen Chemie, 8th edition, system No. 6, page 391 to

400 + supplementary volume (B), page 463 to 465.

Examples of these perchlorates are salts of perchloric acid, anhydrides of perchloric acid with inorganic acids (for example,  $\text{NOClO}_4$ ), organo-metallic perchlorates (for example, trimethyl silyl perchlorate, triphenyl stannyl perchlorate), iodonium perchlorate, tellurium perchlorate, antimonyl perchlorate, thallium perchlorate.

The following examples further illustrate the process of the present invention.

10     Example 1

A mixture of 97.3 parts by weight of trioxane having a water content of less than 20 ppm, 3.0 parts by weight of 1,3-dioxolane and 0.22 part by weight of butylal is continuously fed to a mixing chamber at a temperature of approximately  $70^\circ\text{C}$ , where it is intensely mixed with 0.1 part by weight of a solution of  $\text{HClO}_4$  in dimethyl glycol (1 part by weight of 70% aqueous  $\text{HClO}_4$  in 4500 parts by weight of dimethyl glycol) by means of an impeller. Then, after a retention time of approximately 2 seconds the mixture is fed  
20     into a jacket of propylene, which is folded in the manner shown in Figure 1b. The rate of feed is 12 litres per minute. The polypropylene sheet (having a width of 110 cm and a thickness of 0.2 mm) used for the jacket is unrolled from a roll ahead the point of feeding as a double sheet folded along the centre. The two subjacent edges are bent upwardly at right angles with the aid of two forming jigs (one on the outside and the other on the inside), so that the vertical sheet portion is approximately 10 cm (see Figure 1b). The sheet is then  
30     inclined and passed downwardly into a water bath of 3.50 m length which is heated to  $60^\circ\text{C}$ , so that only the sheet portion which is bent upwardly projects from the bath (like an air intake channel). The jacket and the polymerizing mixture

therein are pulled over a fixed perforated plate in the water at a rate of 1 metre per minute. The perforated plate extends over the entire length of the bath and is pulled upwardly at right angles on one side and thus forms one of the outer baffles for the "air intake channel".

The jacket is further supported by rolls, which are installed at intervals of approximately 20 cm in the direction of travel and which are spring-supported on the upper side, and by the same rolls along the side edge (at 4', Figure 1b) in the manner shown in Figure 1b. The length of the rolls, which are mounted on the top edge always equals the width of the sheet (i.e., 40 cm).

The baffles and guide rolls are so disposed that the polymerizing mixture will have a cross section of approximately 3x40 cm. In the first third of the bath the polymerization has progressed to such an extent that the mixture is rendered turbid by the crystallizing polymer. Vapours escaping during the polymerization are removed through the slot of an exhaust extending over the air intake channel. After passing through the water bath the polymerization is virtually completed and the crude polymer is cooled in a cold-water bath of 6.5 m length following the water bath. Subsequently, the jacket is unfolded and rolled up while the crude polymer is removed sideways, where it falls into a crusher and then into a mill. The crushed crude polymer is boiled with 0.1% ammonium carbonate for 1 hour in order to destroy the catalyst and to remove the non-reacted monomer. At the reaction rate of 82%, a copolymer having the viscosity number  $\eta_{red} = 0.63$  (100 ml/g; dimethyl formamide solution, 135°C) and good thermal stability is obtained. Upon heating under nitrogen for two hours to 220°C, the weight loss is only 2.8 percent. The thermal stability

can be greatly improved by conventional methods, for example, by hydrolytic degradation of the chain ends and by the addition of stabilizers. A product having excellent thermal stability is thus obtained which is especially well suited to producing injection-molded articles. Of course, it is possible to produce copolymers with substantially higher molecular weights by reducing the proportion of regulator (in the present example by reducing the amount of butylal). These copolymers are suitable for extrusion and for the blowing of hollow articles.

The guide device in the cooling bath may also be designed according to the Figures 5 and 6; the perforated plate on which the jacket with the polymerization mixture rests has the reference numeral 33. The thickness of layer of the mixture is adjusted by rolls 30. The rolls 30 are secured to spring-supported brackets 32. The brackets 32 are fastened in turn to supports 31, which can be screwed, for example, to the edge of the trough. The supports 31, the brackets 32 and the rolls 30 are detachable, so that the gap between the rolls can be adjusted arbitrarily. In general, in the initial phase of the polymerization the rolls are mounted at smaller intervals than in the later phases when the polymerization mixture is more solid or even has completely solidified. Figure 6 shows the arrangement according to Figure 5 in the longitudinal direction, showing clearly the different distances between the supports 31.

The remaining reference numerals have the same meanings as in Figs. 1a to 4.

Example 2 (Figure 7 and 8)

A mixture of 180 parts by weight of trioxane having a water content of less than 20 ppm, 7.2 parts by weight of 1,3-dioxepane and 0.2 part by weight of methylal is

continuously pumped into a mixing chamber at 75 to 80°C, where it is intensely mixed with 1 part by weight of a  $\text{BF}_3$  solution (consisting of 1 part by weight of  $\text{BF}_3$ , 8.8 parts by weight of dibutyl ether and 496 parts by weight of 1,2-dichloro ethane) by stirring with an impeller. Then, after a retention time of approximately 2 seconds the mixture is fed (in accordance with Figure 3), through a feed pipe 24 into the space between two endless strips 1 and 2 of glass-fibre-reinforced polytetrafluoro ethylene. The strips have a width of 335 cm and a thickness of 0.35 mm and their marginal zones are jointly bent upwardly. The rate of feed is 8 litres per minute. The two edges of both the lower portion of strip 1 (1') and the upper portion of strip 2 (2') are pulled upwardly by means of rolls 30 attached in the cross direction and by laterally attached baffles, so that the two strips assume the shape of a trough 34, which is open on both sides and the profile of which is evident from Figure 8. This trough 34 is open in the longitudinal direction, i.e., it lacks the two cross walls, and has a length of 1 metre. The strips 1 and 2 with their edges bent upwardly are so inserted in the trough 34 that they are sloping downwardly. When starting the process, a sealing element, for example, a matching piece of sponge rubber wrapped with polyethylene film is placed between the strips, so that the desired filling level can build up. This piece of sponge rubber, which is sealed forwardly because of the shape formed by the strips, is suitably used where the strips enter the trough 34, i.e. at the point where the first trough guide roll touches down (see below). A complete sealing in the forward direction is not possible since the mixture thickens after 10 to 20 seconds. The lower strip 2 subsides into the trough 34 due to the weight of the polymerizing mixture. The upper



strip 1 is pressed downwardly by means of the guide rolls until it is in contact with the surface of the mixture, which is still liquid (see Figure 8). In this manner it is made possible for the polymerization to progress without interference due to atmospheric influences and the evaporation is reduced. The evaporation may be further reduced if the upper strip is cooled, for example, with water. However, cooling or a special temperature bath for the absorption of the polymerization heat is not absolutely necessary. As  
10 Figure 8 shows, it is sufficient if, for example, the jacket is enveloped by the outside air. By the shape of the strips and their mutual distance, the adjusted rate of feed and the rate of removal the polymerizing mixture 7 (Figure 8) obtains a cross section with the average length of approximately 20 cm and a width of 4 cm.

Upon passing the trough 34 the strips with the solidified content are pulled over rolls 35 (Figure 7) and the upturned edges are reconverted into the horizontal shape by means of laterally attached side plates. The strips are  
20 passed over the guide rolls 37. The strips are removed by take-up rolls 39. Residues of monomers or polymers adhering to the strips are removed by means of scrapers or brushes. The effective length of the apparatus is, for example, 6 metres and the rate of removal is 1 metre per minute.

If a chain conveyer which is open on both sides (front and rear) and the members of which have the shape of the trough is used instead of the trough 9 and some of the rolls (Figure 7), then it is possible to reduce the stretching strain of the polytetrafluoro ethylene strip and the wear due  
30 to friction, which is encountered in extended operations.

The polymer drops over a chute 40 into conveyer baskets and in order to complete the reaction, it is tempered

at 80°C for approximately 15 minutes prior to the crushing.  
The further treatment is similar to that described in  
example 1. At a reaction rate of 80.5 percent, a copolymer  
having the viscosity number  $\eta_{red}=0.61$  is obtained. After  
5 2 hours of heating under nitrogen to 220°C its weight loss  
is 2.1 percent.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for producing homopolymers or copolymers by the continuous polymerization of a polymerization mixture using polymerization initiators comprising the steps of continuously feeding the polymerization mixture into a continuously moving jacket of a flexible material with substantially complete displacement of air; folding the side edges of said jacket to form a closed compartment for said polymerization mixture; passing said jacket through a zone at the polymerization temperature to effect polymerization of said mixture, said polymerization mixture containing a cyclic compound having at least one C-O-C bond in the ring or a linear polymeric compound having C-O-C bonds.

2. A process according to claim 1, wherein said polymerization mixture contains at least one of cyclic acetals and linear polyacetals.

3. A process according to claim 1, wherein the polymerization mixture contains trioxane or tetroxane.

4. A process according to claim 1, wherein a very active cationic initiator is present in said polymerization mixture.

5. A process according to claim 4, wherein at least one of perchloric acid, perchloric esters and perchloric anhydrides is used as the initiator.



ABSTRACT OF THE DISCLOSURE

A polymerization mixture for producing homopolymers or copolymers by continuous polymerization and containing a cyclic compound having at least one C-O-C bond in the ring or a linear polymeric compound having C-O-C bonds is continuously polymerized by injecting the mixture into a continuously moving jacket formed from a single sheet folded over on itself or by a pair of sheets. The side edges of the sheet(s) are folded to close the jacket, which is passed through a heated polymerization zone to effect polymerization.